

Computer Simulation of Quantum Dynamics in a Classical Spin Environment

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In this paper a formalism for studying the dynamics of quantum systems coupled to classical spin environments is reviewed. The theory is based on generalized antisymmetric brackets and naturally predicts open-path off-diagonal geometric phases in the evolution of the density matrix. It is shown that such geometric phases must also be considered in the quantum-classical Liouville equation for a classical bath with canonical phase space coordinates; this occurs whenever the adiabatic basis is complex (as in the case of a magnetic field coupled to the quantum subsystem). When the quantum subsystem is weakly coupled to the spin environment, non-adiabatic transitions can be neglected and one can construct an effective non-Markovian computer simulation scheme for open quantum system dynamics in classical spin environments. In order to tackle this case, integration algorithms based on the symmetric Trotter factorization of the classical-like spin propagator are derived. Such algorithms are applied to a model comprising a quantum two-level system coupled to a single classical spin in an external magnetic field. Starting from an excited state, the population difference and the coherences of this two-state model are simulated in time while the dynamics of the classical spin is monitored in detail. It is the author's opinion that the numerical evidence provided in this paper is a first step toward developing the simulation of quantum dynamics in classical spin environments into an effective tool. In turn, the ability to simulate such a dynamics can have a positive impact on various fields, among which, for example, nano-science.

I. INTRODUCTION

The computer simulation of systems of interest to nano-science requires to consider in detail the environment surrounding, for example, the quantum reactive centers [1], the Josephson junctions [2] or the quantum dots [3–5]. Environments can be represented either by means of bosonic degrees of freedom [6] or by spinors [7] (or also by a combination of the two types of coordinates). In practice, following accurately the dynamics of both the relevant system and the surrounding environment (bath) leads to a theoretical/computational approach that is complementary to the study of master equations [8–14].

A scheme to perform the computer simulation of quantum systems coupled to classical spin baths was introduced in [15]. The approach of Ref. [15] can be classified within the quantum-classical approximations [16–20] to quantum dynamics since it is based on a quantum-classical Liouville equation [21–27] for a classical spin bath. It is interesting that the formalism in [15] does not require to approximate the memory function of the environment since the bath degrees of freedom are described explicitly, in the spirit of molecular dynamics simulations [28, 29]. From this point of view, the approach of Ref. [15] provides a non-Markovian route to the simulation of quantum effects in classical spin baths. It is worthy of note that the formalism in [15] was naturally devised exploiting the mathematical structure provided by generalized antisymmetric brackets [30–32]. Such brackets have also been used to formulate the statistical mechanics of systems with thermodynamic [33–35] and holonomic constraints [36, 37] in classical mechanics.

In the regime of weak coupling, the adiabatic basis is particularly suited for numerical studies. When such a basis is complex (*e.g.*, in the presence of magnetic dipoles and fields), it has been shown that the formalism of Ref. [15] naturally predicts an open [38, 39] geometric phase [40–43] in the evolution of the off-diagonal matrix elements of operators.

In this paper, three topics will be dealt with. The first is that, when the adiabatic basis is complex, also the quantum-classical Liouville equation in a classical bath with canonical (position/momentum) coordinates possesses an open geometric phase term for the off-diagonal matrix elements. The second is a brief review of the formalism for the quantum dynamics of systems in classical spin baths, as introduced in Ref. [15]. The third is the explicit

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formulation of integration algorithms, based on the symmetric Trotter factorization [44–46] of the classical spin propagator. It is worth noting that the classical-like spin dynamics could also have been integrated by means of the elegant measure-preserving algorithms invented by Gregory Ezra [47–49]. In order to illustrate the algorithms, a specific model comprising a quantum two-level system coupled to a classical spin is studied and numerical results are reported. It is the author’s opinion that the numerical algorithms presented here are a first significant step toward developing the theory introduced in Ref. [15] into an effective tool for studying quantum nano-systems.

This paper is organized as follow. In Sec. II the formulation of quantum-classical dynamics of quantum systems in environments represented by canonically conjugate variables is summarized. It is shown that, when the basis is complex, one has to consider a geometric phase in the evolution of the off-diagonal matrix elements also in this case. In Sec. III it is briefly reviewed how the quantum-classical theory of Sec. II can be generalized to describe quantum systems in classical spin baths. The model system simulated in this paper is introduced in Sec. IV. Its time-reversible integrators, on the various energy surfaces, are developed in Sec. V. The detailed algorithms for integration on the (1, 1), (2, 2) and (1, 2) surfaces are given in the Appendices A-C. The details and the results of the calculations on the model are discussed in Sec. VI. Finally, conclusions and perspectives are given in Sec. VII.

II. QUANTUM-CLASSICAL LIOUVILLE EQUATION IN A COMPLEX ADIABATIC BASIS

Consider a quantum system whose Hamiltonian operator $\hat{H}(\{\xi\})$ is defined in terms of a set of quantum operators $\hat{\xi}_i$, $i = 1, \dots, n$ and assume that the quantum degrees of freedom interact with a classical bath which can be represented by canonical phase space coordinates $X = (R, P)$. Such classical coordinates enter the definition of the bath classical Hamiltonian $H_B(X)$. It is worth stating clearly that in this section a multidimensional notation is adopted. According to this, for example, the symbol R stands for (R_1, R_2, \dots) , and a scalar products such as $P \cdot P$ stand for $\sum_I P_I^2$. Such a multidimensional notation will be abandoned in favor of a more explicit notation in the next sections. The interaction between the quantum subsystem and the classical bath is given in terms of a coupling term $\hat{H}_C(\{\xi\}, X)$. The total Hamiltonian (which must be a constant of motion) describing the coupled quantum subsystem plus classical bath can be written as

$$\hat{\mathcal{H}}(X) = \hat{H}(\{\xi\}) + \hat{H}_C(\{\xi\}, X) + H_B(X). \quad (1)$$

Accordingly, one is also led to introduce a quantum-classical density matrix $\hat{\rho}_{\text{QC}}(X)$ and quantum-classical operators $\hat{\chi}_{\text{QC}}(X)$. The evolution in time, in a Schrödinger-like dynamical picture can be postulated as

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{\text{QC}}(X, t) &= -\frac{i}{\hbar} \left[\hat{\mathcal{H}}(X) \hat{\rho}_{\text{QC}}(X, t) \right] \mathcal{D} \begin{bmatrix} \hat{\mathcal{H}}(X) \\ \hat{\rho}_{\text{QC}}(X, t) \end{bmatrix}, \\ &= -\frac{i}{\hbar} \left[\hat{\mathcal{H}}(X), \hat{\rho}_{\text{QC}}(X, t) \right]_{\mathcal{D}}. \end{aligned} \quad (2)$$

In Equation (2) the antisymmetric matrix operator \mathcal{D} has been introduced. It is defined as

$$\mathcal{D} = \begin{bmatrix} 0 & 1 + \frac{i\hbar}{2} \overleftarrow{\frac{\partial}{\partial X_I}} \mathcal{B}_{IJ} \overrightarrow{\frac{\partial}{\partial X_J}} \\ -1 - \frac{i\hbar}{2} \overleftarrow{\frac{\partial}{\partial X_I}} \mathcal{B}_{IJ} \overrightarrow{\frac{\partial}{\partial X_J}} & 0 \end{bmatrix}, \quad (3)$$

where

$$\mathcal{B} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad (4)$$

is the symplectic matrix. The arrows over the partial derivative symbols in Eq. (2) denote in which direction the partial derivative operator must act. Moreover, in Eq. (2) and in the following the sum over repeated indices is implied. Equation (2), which is just the quantum-classical Liouville equation [21–27] written in matrix form, defines what is known as quantum-classical bracket [16–20] or non-Hamiltonian commutator [30]. The bracket couples the dynamics of the phase space degrees of freedom with that of the quantum operators; it takes into account both the conservation of the energy and the quantum back-reaction. Moreover, when there is no coupling, i.e., $\hat{H}_C = 0$, the bracket makes the quantum system evolve in terms of the standard quantum commutator and the classical bath through the Poisson bracket.

The quantum-classical bracket in Eq. (2) does not satisfy the Jacobi relation and this, in turn, leads to the lack of time-translation invariance of the algebra defined in terms of the bracket itself [30, 50]. Less abstract consequences

of such mathematical features are that the coordinates of the bath, which are classical at time zero, acquire quantum phases as time flows. With respect to this, one has to consider the bracket as an approximation to the correct quantum dynamics of the total system (subsystem plus bath). Such a dynamics, although correct in principle, would not be calculable so that, following the philosophy of *approximated theoretical complexity* (as discussed in [51]), the quantum-classical bracket can be invoked as an effective tool in order to perform computer simulations that would be otherwise impossible. In practice, fast bath decoherence may alleviate the theoretical problems associated with the acquisition of quantum phase terms by the variables that should stay classical and, indeed, the quantum-classical bracket, or quantum-classical Liouville equation, is used for many applications in chemistry and physics [16–27]. It is worth reminding that the non-Lie (or, as they are also called, non-Hamiltonian) brackets, with their lack of time translation invariance, are also used as technical tools to impose thermodynamical (such as constant temperature and/or pressure) [33–35] and holonomic constraints [36, 37] in classical molecular dynamics calculations [28, 29].

The abstract equations of motion in (2) can be represented in the adiabatic basis. Upon writing the total Hamiltonian as $\hat{\mathcal{H}}(X) = (P^2/2M) + \hat{h}(R)$, such a basis is defined by the eigenvalue problem $\hat{h}(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$. In the adiabatic basis the quantum-classical evolution reads

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{\alpha\alpha'}(X, t) = & - \sum_{\beta\beta'} [i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} \\ & + J_{\alpha\alpha',\beta\beta'}] \hat{\rho}_{\beta\beta'}(X, t) . \end{aligned} \quad (5)$$

In Equation (5) the symbol $\omega_{\alpha\alpha'}(R) = [E_\alpha(R) - E_{\alpha'}(R)]/\hbar$ denotes the Bohr frequency,

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2} (F_W^\alpha + F_W^{\alpha'}) \cdot \frac{\partial}{\partial P} , \quad (6)$$

is the classical-like Liouville operator for the bath degrees of freedom, $F_W^\alpha = -\langle\alpha; R|(\partial\hat{h}/\partial R)|\alpha; R\rangle$ is the Hellmann-Feynman force, and

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} = & \frac{P}{M} \cdot d_{\alpha\beta} \left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} \\ & + \frac{P}{M} \cdot d_{\alpha'\beta'}^* \left(1 + \frac{1}{2} S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta} , \end{aligned} \quad (7)$$

is the transition operator, responsible for the non-adiabatic transitions between the energy levels of the quantum subsystem, as a result of the coupling to the bath. The symbol $d_{\alpha\beta} = \langle\alpha|\partial/\partial R|\beta\rangle$ denotes the non-adiabatic coupling vector. In Equation (7), the vector $S_{\alpha\beta} = \hat{d}_{\alpha\beta}(E_\alpha - E_\beta)(\hat{d}_{\alpha\beta} \cdot P/M)^{-1}$ together with its complex conjugate $S_{\alpha'\beta'}^*$, have been defined (the symbol $\hat{d}_{\alpha\beta}$ denotes the normalization of the coupling vector over the space of all R coordinates).

The coupling vector has the property $d_{\alpha\beta} = -d_{\beta\alpha}^*$ so that, when the adiabatic basis is real, $d_{\alpha\alpha} = 0$ and the transition operator in eq. (7) is purely off-diagonal. However, when the basis is complex (e.g., when the symmetry under time-inversion is broken, for example, because of a magnetic field), $d_{\alpha\alpha}$ is not zero and is purely imaginary

$$d_{\alpha\alpha} = i\phi_{\alpha\alpha} \neq 0 . \quad (8)$$

One can see that a phase $\phi_{\alpha\alpha}$ is naturally emerging from the representation of the quantum-classical Liouville equation in a complex basis. Hence, in a complex adiabatic basis, Eq. (5) can be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{\alpha\alpha'}(X, t) = & - \sum_{\beta\beta'} \left[i\omega_{\alpha\alpha'} + i\frac{P}{M} (\phi_{\alpha\alpha} - \phi_{\alpha'\alpha'}) \right. \\ & \left. + iL_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'}^{\text{od}} \right] \hat{\rho}_{\beta\beta'}(X, t) . \end{aligned} \quad (9)$$

where $J_{\alpha\alpha',\beta\beta'}^{\text{od}}$ is the off-diagonal part of the transition operator

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'}^{\text{od}} = & \frac{P}{M} \cdot d_{\alpha\beta} [1 - \delta_{\alpha\beta}] \left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} \\ & + \frac{P}{M} \cdot d_{\alpha'\beta'}^* [1 - \delta_{\alpha'\beta'}] \left(1 + \frac{1}{2} S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta} , \end{aligned} \quad (10)$$

While the phase $\omega_{\alpha\alpha}$ has a dynamical source, the phase $\phi_{\alpha\alpha}$ has a geometric origin and it is analogous to the famous Berry phase [40–42]. Hence, Equation (9) is the quantum-classical Liouville equation displaying geometric phase effects. In principle, such phases are also present for open paths [52] of the classical environment and they are off-diagonal in nature [53–55].

III. QUANTUM-CLASSICAL SPIN DYNAMICS

Consider a classical spin vector \mathbf{S} with components S_I , $I = x, y, z$, whose energy is described by the Hamiltonian be $H_{\text{SB}}(\mathbf{S})$. It is known that the equations of motion can be written in matrix form as

$$\dot{S}_I = \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\text{SB}}}{\partial S_J}, \quad (11)$$

where

$$\mathcal{B}^{\text{S}} = \begin{bmatrix} 0 & S_z & -S_y \\ -S_z & 0 & S_x \\ S_y & -S_x & 0 \end{bmatrix}. \quad (12)$$

The antisymmetric matrix \mathcal{B}^{S} can also be written in a compact way as

$$\mathcal{B}_{IJ}^{\text{S}} = \epsilon_{IJK} S_K. \quad (13)$$

The equations of motion (11) preserve the Casimir $C_2 = \mathbf{S} \cdot \mathbf{S}$ for any arbitrary Hamiltonian $H_{\text{SB}}(\mathbf{S})$. They also have a zero phase space compressibility

$$\kappa = \frac{\partial \dot{S}_I}{\partial S_I} \epsilon_{IJK} \delta_{KJ} \frac{\partial H_{\text{SB}}}{\partial S_J} + \mathcal{B}_{IJ}^{\text{S}} \frac{\partial^2 H_{\text{SB}}}{\partial S_I \partial S_J} = 0. \quad (14)$$

The equations of motion can also be written in the form

$$\dot{S}_I = \{S_I, H_{\text{SB}}\}_{\mathcal{B}^{\text{S}}}, \quad (15)$$

upon introducing a non-canonical bracket defined as

$$\{A, B\}_{\mathcal{B}^{\text{S}}} = \frac{\partial A}{\partial S_I} \mathcal{B}_{IJ}^{\text{S}} \frac{\partial B}{\partial S_J}, \quad (16)$$

where $A = A(\mathbf{S})$ and $B = B(\mathbf{S})$ are arbitrary functions of the spin degrees of freedom.

Let us assume that the classical spin system is interacting with the quantum system with Hamiltonian operator $\hat{H}(\{\hat{\chi}\})$ through an interaction of the form $\hat{H}_c(\{\hat{\chi}\}, \mathbf{S})$. The total Hamiltonian operator of the quantum subsystem in the classical spin bath can be written analogously to Eq. (1)

$$\hat{\mathcal{H}}(\mathbf{S}) = \hat{H}(\{\hat{\chi}\}) + \hat{H}_c(\{\hat{\chi}\}, \mathbf{S}) + H_{\text{SB}}(\mathbf{S}). \quad (17)$$

The evolution of the density matrix $\hat{\rho}(\mathbf{S})$ of the quantum system in the classical bath can be postulated in the form

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(\mathbf{S}, t) &= -\frac{i}{\hbar} [\hat{\mathcal{H}}(\mathbf{S}), \hat{\rho}(\mathbf{S}, t)] \cdot \mathcal{D}^{\text{S}} \cdot \begin{bmatrix} \hat{\mathcal{H}}(\mathbf{S}) \\ \hat{\rho}(\mathbf{S}, t) \end{bmatrix}, \\ &= -\frac{i}{\hbar} [\hat{\mathcal{H}}(\mathbf{S}), \hat{\rho}(\mathbf{S}, t)]_{\mathcal{D}^{\text{S}}} \end{aligned} \quad (18)$$

where

$$\mathcal{D}^{\text{S}} = \begin{bmatrix} 0 & 1 + \frac{i\hbar}{2} \overleftarrow{\frac{\partial}{\partial S_I}} \mathcal{B}_{IJ}^{\text{S}} \overrightarrow{\frac{\partial}{\partial S_J}} \\ -1 - \frac{i\hbar}{2} \overleftarrow{\frac{\partial}{\partial S_I}} \mathcal{B}_{IJ}^{\text{S}} \overrightarrow{\frac{\partial}{\partial S_J}} & 0 \end{bmatrix}. \quad (19)$$

The right-hand side of Eq. (18) introduces a quantum-classical bracket for a quantum subsystem in a classical spin bath.

In order to represent the abstract Eq. (18) the quantum-classical Hamiltonian of Eq. (17) can be rewritten as

$$\hat{\mathcal{H}}(\mathbf{S}) = \hat{h}(\mathbf{S}) + H_{\text{SB}}(\mathbf{S}) . \quad (20)$$

Accordingly, the adiabatic basis is defined by the eigenvalue equation

$$\hat{h}(\mathbf{S})|\alpha; \mathbf{S}\rangle = E_\alpha(\mathbf{S})|\alpha; \mathbf{S}\rangle . \quad (21)$$

However, at variance with the case of the canonical coordinate bath discussed in Sec. II, where it depended only on the positions R (and not on the conjugate momenta P), the adiabatic basis defined by Eq. (21) depends on all the non-canonical spin coordinates \mathbf{S} . Hence, in the spin adiabatic basis, Eq. (18) becomes

$$\begin{aligned} \partial_t \rho_{\alpha\alpha'} &= -i\omega_{\alpha\alpha'} \rho_{\alpha\alpha'} - \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\text{SB}}}{\partial S_J} \langle \alpha; \mathbf{S} | \frac{\partial \hat{\rho}}{\partial S_I} | \alpha'; \mathbf{S} \rangle \\ &+ \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \langle \alpha; \mathbf{S} | \frac{\partial \hat{h}}{\partial S_I} \frac{\partial \hat{\rho}}{\partial S_J} | \alpha'; \mathbf{S} \rangle \\ &- \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \langle \alpha; \mathbf{S} | \frac{\partial \hat{\rho}}{\partial S_I} \frac{\partial \hat{h}}{\partial S_J} | \alpha'; \mathbf{S} \rangle , \end{aligned} \quad (22)$$

where the antisymmetry of \mathcal{B}^{S} has been used. As it was done in Sec. II, a coupling vector can be defined as

$$d_{\sigma\alpha}^I = \langle \sigma; \mathbf{S} | \frac{\partial}{\partial S_I} | \alpha; \mathbf{S} \rangle , \quad (23)$$

where the index I of the spin components has been left explicit. The following identities can be easily found

$$\begin{aligned} \langle \alpha; \mathbf{S} | \frac{\partial \hat{\rho}}{\partial S_I} | \alpha'; \mathbf{S} \rangle &= \frac{\partial \rho_{\alpha\alpha'}}{\partial S_I} + d_{\alpha\sigma}^I \rho_{\sigma\alpha'} \\ &- \rho_{\alpha\sigma'} d_{\sigma'\alpha'}^I , \end{aligned} \quad (24)$$

$$\langle \alpha; \mathbf{S} | \frac{\partial \hat{h}}{\partial S_I} | \sigma; \mathbf{S} \rangle = \frac{\partial h_{\alpha\sigma}}{\partial S_I} - \Delta E_{\alpha\sigma} d_{\alpha\sigma}^I , \quad (25)$$

where $\Delta E_{\alpha\sigma} = E_\alpha - E_\sigma$. With the help of Eqs. (24) and (25), the equations of motion can be written as

$$\begin{aligned} \partial_t \rho_{\alpha\alpha'} &= -i\omega_{\alpha\alpha'} \rho_{\alpha\alpha'} - \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\text{SB}}}{\partial S_J} \frac{\partial \rho_{\alpha\alpha'}}{\partial S_I} - \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \frac{\partial E_\alpha}{\partial S_J} \frac{\partial \rho_{\alpha\alpha'}}{\partial S_I} \\ &- \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \frac{\partial E_{\alpha'}}{\partial S_J} \frac{\partial \rho_{\alpha\alpha'}}{\partial S_I} - \left(-\mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\text{SB}}}{\partial S_J} d_{\alpha\beta}^I \delta_{\alpha'\beta'} \right. \\ &- \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\text{SB}}}{\partial S_J} d_{\alpha'\beta'}^{I*} \delta_{\alpha\beta} - \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \Delta E_{\alpha\beta} d_{\alpha\beta}^I \frac{\partial}{\partial S_J} \delta_{\alpha'\beta'} \\ &- \left. \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \Delta E_{\alpha'\beta'} d_{\beta'\alpha'}^{I*} \frac{\partial}{\partial S_J} \delta_{\alpha\beta} \right) \rho_{\beta\beta'} \\ &+ \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \left(\frac{\partial E_\alpha}{\partial S_I} d_{\alpha\beta}^J \delta_{\alpha'\beta'} - \frac{\partial E_\alpha}{\partial S_I} d_{\beta'\alpha'}^J \delta_{\alpha\beta} \right. \\ &- \Delta E_{\alpha\sigma} d_{\alpha\sigma}^I d_{\sigma\beta}^J \rho_{\beta\alpha'} + \Delta E_{\alpha\beta} d_{\alpha\beta}^I d_{\beta'\alpha'}^J \left. \right) \rho_{\beta\beta'} \\ &- \frac{1}{2} \mathcal{B}_{IJ}^{\text{S}} \left(\frac{\partial E_{\alpha'}}{\partial S_J} d_{\alpha\beta}^I \delta_{\alpha'\beta'} - \frac{\partial E_{\alpha'}}{\partial S_J} d_{\beta'\alpha'}^I \delta_{\alpha\beta} \right. \\ &+ \left. \Delta E_{\sigma'\alpha'} d_{\sigma'\alpha'}^J d_{\beta'\sigma'}^I \delta_{\alpha\beta} - \Delta E_{\beta'\alpha'} d_{\beta'\alpha'}^J d_{\alpha\beta}^I \right) \rho_{\beta\beta'} . \end{aligned} \quad (26)$$

At this stage, it is useful to introduce a classical-like spin-Liouville operator:

$$\begin{aligned} L_{\alpha\alpha'} &= \left(\mathcal{B}_{IJ}^S \frac{\partial H_{SB}}{\partial S_J} \frac{\partial}{\partial S_I} + \frac{1}{2} \mathcal{B}_{IJ}^S \frac{\partial E_{\alpha'}}{\partial S_J} \frac{\partial}{\partial S_I} + \frac{1}{2} \mathcal{B}_{IJ}^S \frac{\partial E_{\alpha}}{\partial S_J} \frac{\partial}{\partial S_I} \right) \\ &= \mathcal{B}_{IJ}^S \frac{\partial H_{\alpha\alpha'}}{\partial S_J} \frac{\partial}{\partial S_I} = \{ \dots, H_{\alpha\alpha'}^S \}_{\mathbf{S}^S}, \end{aligned} \quad (27)$$

where the matrix elements of the total system Hamiltonian on the adiabatic surfaces are denoted as

$$H_{\alpha\alpha'}^S = H_{SB} + \frac{1}{2} (E_{\alpha} + E_{\alpha'}) . \quad (28)$$

A transition operator for the spin bath can be defined as

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} &= \mathcal{B}_{IJ}^S \frac{\partial H_{SB}}{\partial S_J} d_{\alpha\beta}^I \delta_{\beta'\alpha'} + \frac{1}{2} \mathcal{B}_{IJ}^S \Delta E_{\alpha\beta} d_{\alpha\beta}^I \frac{\partial}{\partial S_J} \delta_{\alpha'\beta'} \\ &+ \mathcal{B}_{IJ}^S \frac{\partial H_{SB}}{\partial S_J} d_{\alpha'\beta'}^{I*} \delta_{\alpha\beta} + \frac{1}{2} \mathcal{B}_{IJ}^S \Delta E_{\alpha'\beta'} d_{\alpha'\beta'}^{I*} \frac{\partial}{\partial S_J} \delta_{\alpha\beta} . \end{aligned} \quad (29)$$

The operator in Eq. (29) goes to the transition operator in Eq.(10) when canonical variables are considered. In the case of a spin bath, in order to take properly into account non-adiabatic effects, a higher order transition operator (acting together with $J_{\alpha\alpha',\beta\beta'}$) must be considered. Such an operator is

$$\begin{aligned} \mathcal{S}_{\alpha\alpha',\beta\beta'} &= \frac{1}{2} \mathcal{B}_{IJ}^S \frac{\partial (E_{\alpha} + E_{\alpha'})}{\partial S_I} d_{\alpha\beta}^J \delta_{\alpha'\beta'} \\ &+ \frac{1}{2} \mathcal{B}_{IJ}^S \frac{\partial (E_{\alpha} + E_{\alpha'})}{\partial S_I} d_{\alpha'\beta'}^{J*} \delta_{\alpha\beta} \\ &- \frac{1}{2} \mathcal{B}_{IJ}^S \Delta E_{\alpha\sigma} d_{\alpha\sigma}^I d_{\sigma\beta}^J \delta_{\beta\alpha'} - \frac{1}{2} \mathcal{B}_{IJ}^S \Delta E_{\alpha\beta} d_{\alpha\beta}^I d_{\alpha'\beta'}^{J*} \\ &- \frac{1}{2} \mathcal{B}_{IJ}^S \Delta E_{\alpha'\sigma'} d_{\alpha'\sigma'}^{I*} d_{\sigma'\beta'}^{J*} \delta_{\alpha\beta} \\ &- \frac{1}{2} \mathcal{B}_{IJ}^S \Delta E_{\alpha'\beta'} d_{\alpha'\beta'}^{I*} d_{\alpha\beta}^J . \end{aligned} \quad (30)$$

The operator in Eq. (30) is identically zero for canonical conjugate variables. Using Eqs. (27-30), the equation of motion reads

$$\begin{aligned} \partial_t \rho_{\alpha\alpha'} &= \sum_{\beta\beta'} \left(-i\omega_{\alpha\alpha'} \delta_{\alpha\beta} \delta_{\alpha\alpha'} - L_{\alpha\alpha'} \delta_{\alpha\beta} \delta_{\alpha\alpha'} - J_{\alpha\alpha',\beta\beta'} \right. \\ &\left. + \mathcal{S}_{\alpha\alpha',\beta\beta'} \right) \rho_{\beta\beta'} . \end{aligned} \quad (31)$$

The general equations of motion (31) are difficult to integrate if one desires to take into account non-adiabatic corrections. However, in the case of weak coupling between the spin bath and the quantum subsystem, one is allowed to take the adiabatic limit of the operators in Eqs. (29) and (30). This is performed by assuming that the off-diagonal elements of $d_{\alpha\alpha'}$ (which couple different adiabatic energy surfaces) are negligible. In such a case, one obtains

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'}^{\text{ad}} &= -\mathcal{B}_{IJ}^S \frac{\partial H_{SB}}{\partial S_J} (d_{\alpha\alpha}^I + d_{\alpha'\alpha'}^{I*}) \delta_{\alpha\beta} \delta_{\beta'\alpha'} \\ &= -i\mathcal{B}_{IJ}^S \frac{\partial H_{SB}}{\partial S_J} (\Phi_{\alpha\alpha}^I - \Phi_{\alpha'\alpha'}^I) \delta_{\alpha\beta} \delta_{\beta'\alpha'} , \end{aligned} \quad (32)$$

where, using the fact that $d_{\alpha\alpha}^I$ is purely imaginary, a phase

$$\Phi_{\alpha\alpha'}^I = -i d_{\alpha\alpha'}^I \quad (33)$$

has been introduced in a manner analogous to that when the bath has a representation in terms of canonical variables. In a similar way, one can take the adiabatic limit of the $\mathcal{S}_{\alpha\alpha',\beta\beta'}$ in Eq. (30):

$$\mathcal{S}_{\alpha\alpha',\beta\beta'}^{\text{ad}} = -\frac{i}{2}\mathcal{B}_{IJ}^{\text{S}} \frac{\partial(E_{\alpha} + E_{\alpha'})}{\partial S_J} (\Phi_{\alpha\alpha}^I - \Phi_{\alpha'\alpha'}^I) \delta_{\alpha\alpha} \delta_{\alpha'\alpha'} . \quad (34)$$

Hence, in the weak-coupling (adiabatic) limit, the equation of motion reads

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{\alpha\alpha'} = & \left[-i\omega_{\alpha\alpha'} - i\mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\alpha\alpha'}^{\text{S}}}{\partial S_J} (\Phi_{\alpha\alpha}^I - \Phi_{\alpha'\alpha'}^I) \right. \\ & \left. - \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\alpha\alpha'}^{\text{S}}}{\partial S_J} \frac{\partial}{\partial S_I} \right] \rho_{\alpha\alpha'} . \end{aligned} \quad (35)$$

In the absence of explicit time-dependence in the basis set, Eq. (35) can be rewritten as

$$\begin{aligned} \partial_t \rho_{\alpha\alpha'} = & \left[-i\omega_{\alpha\alpha'} - \left(\langle \alpha, \mathbf{S} | \frac{d}{dt} | \alpha, \mathbf{S} \rangle - \langle \alpha', \mathbf{S} | \frac{d}{dt} | \alpha', \mathbf{S} \rangle \right) \right. \\ & \left. - \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\alpha\alpha'}^{\text{S}}}{\partial S_J} \frac{\partial}{\partial S_I} \right] \rho_{\alpha\alpha'} . \end{aligned} \quad (36)$$

Using the Dyson identity, this can be written in propagator form as

$$\begin{aligned} \rho_{\alpha\alpha'}(t) = & \exp \left[-i \int_{t_0}^t dt' \omega_{\alpha\alpha'}(t') \right] \\ & \times \exp \left[- \int_{t_0}^t dt' \left(\langle \alpha, \mathbf{S} | \frac{d}{dt'} | \alpha, \mathbf{S} \rangle - \langle \alpha', \mathbf{S} | \frac{d}{dt'} | \alpha', \mathbf{S} \rangle \right) \right] \\ & \times \exp \left[-(t - t_0) \mathcal{B}_{IJ}^{\text{S}} \frac{\partial H_{\alpha\alpha'}^{\text{S}}}{\partial S_J} \frac{\partial}{\partial S_I} \right] \rho_{\alpha\alpha'}(t_0) . \end{aligned} \quad (37)$$

Equation (37) provides the adiabatic approximation of the quantum-classical Liouville equations in spin baths. The geometric phase arise from the time integral of the term $\langle \alpha, \mathbf{S} | (d/dt) | \alpha, \mathbf{S} \rangle - \langle \alpha', \mathbf{S} | (d/dt) | \alpha', \mathbf{S} \rangle$, which is purely off-diagonal.

IV. QUANTUM-CLASSICAL SPIN MODEL

Consider a quantum two-level system represented by the Pauli matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad (38)$$

and a classical spin with components $\mathbf{S} = (S_x, S_y, S_z)$ immersed in a constant magnetic field $\mathbf{B} = (0, 0, b)$. Hence, consider a model defined by the total Hamiltonian below

$$\begin{aligned} \hat{H}(\mathbf{S}) = & -\Omega \sigma_x - c_1 b \sigma_z - \mu \mathbf{S} \cdot \boldsymbol{\sigma} - c_2 b S_z + \frac{S_z^2}{2} \\ = & \hat{h}(\mathbf{S}) - c_2 b S_z + \frac{S_z^2}{2}, \end{aligned} \quad (39)$$

where $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$, and c_1, c_2 are coupling coefficients.

Upon defining

$$\gamma = c_1 b + \mu S_z, \quad (40)$$

$$\eta = -\mu S_y, \quad (41)$$

$$\tilde{\Omega} = \Omega + \mu S_x, \quad (42)$$

one can write the eigenvalues of the Hamiltonian (39) as

$$E_1 = +\sqrt{\tilde{\Omega}^2 + \gamma^2 + \eta^2}, \quad (43)$$

$$E_2 = -\sqrt{\tilde{\Omega}^2 + \gamma^2 + \eta^2}, \quad (44)$$

and the eigenvectors as

$$|E_1\rangle = \frac{1}{\sqrt{2(1+|\tilde{G}|^2)}} \begin{pmatrix} 1 + \tilde{G}^* \\ \tilde{G} - 1 \end{pmatrix}, \quad (45)$$

$$|E_2\rangle = \frac{1}{\sqrt{2(1+|\tilde{G}|^2)}} \begin{pmatrix} 1 - \tilde{G}^* \\ 1 + \tilde{G} \end{pmatrix}, \quad (46)$$

where $\tilde{G} = G + i\eta/\gamma$, and

$$G = \frac{-\tilde{\Omega} + \sqrt{\tilde{\Omega}^2 + \gamma^2 + \eta^2}}{\gamma}. \quad (47)$$

A. Dynamics on the adiabatic surfaces

In a Heisenberg-like picture of the dynamics, quantum-classical operators $\hat{\chi}(\mathbf{S}, t)$, depending on the classical spin coordinates, evolve in time while the density matrix remain stationary. From the equation of motion for the density matrix given in (37), one can easily obtain the evolution equation for the operator in the adiabatic basis. For clarity, it is useful to write it explicitly

$$\begin{aligned} \chi_{\alpha\alpha'}(t) &= \exp \left[i \int_{t_0}^t dt' \omega_{\alpha\alpha'}(t') \right] \\ &\times \exp \left[\int_{t_0}^t dt' \left(\langle \alpha, S | \frac{d}{dt'} | \alpha, S \rangle - \langle \alpha', S | \frac{d}{dt'} | \alpha', S \rangle \right) \right] \\ &\times \exp \left[(t - t_0) \mathcal{B}_{IJ}^S \frac{\partial H_{\alpha\alpha'}^S}{\partial S_J} \frac{\partial}{\partial S_I} \right] \chi_{\alpha\alpha'}(t_0). \end{aligned} \quad (48)$$

The equation of motion (48) can be simulated on the computer in terms of classical-like trajectories evolving on adiabatic energy surfaces. The classical-like spin Liouville operator defined in (27) determines the equations of motion

$$\dot{S}_x = S_z \frac{\partial H_{\alpha\alpha'}}{\partial S_y} - S_y \frac{\partial H_{\alpha\alpha'}}{\partial S_z}, \quad (49)$$

$$\dot{S}_y = -S_z \frac{\partial H_{\alpha\alpha'}}{\partial S_x} + S_x \frac{\partial H_{\alpha\alpha'}}{\partial S_z}, \quad (50)$$

$$\dot{S}_z = S_y \frac{\partial H_{\alpha\alpha'}}{\partial S_x} - S_x \frac{\partial H_{\alpha\alpha'}}{\partial S_y}, \quad (51)$$

where $H_{\alpha\alpha'}$ are the adiabatic surface Hamiltonians. For the model in Eq. (39), these can be written explicitly as

$$H_{11} = \frac{S_z^2}{2} - c_2 b S_z + \sqrt{\tilde{\Omega}^2 + \gamma^2 + \eta^2}, \quad (52)$$

$$H_{12} = H_{21} = \frac{S_z^2}{2} - c_2 b S_z, \quad (53)$$

$$H_{22} = \frac{S_z^2}{2} - c_2 b S_z - \sqrt{\tilde{\Omega}^2 + \gamma^2 + \eta^2}, \quad (54)$$

where γ , η and $\tilde{\Omega}$ have been defined in Eqs. (40-42).

In order to write explicitly the equations of motion for the spin onto the three energy surfaces, one needs to calculate the derivatives of the Hamiltonians H_{11} , H_{12} and H_{22} with respect to the spin components (S_x, S_y, S_z) . On the (1, 1) surface one finds:

$$\frac{\partial H_{11}}{\partial S_x} = \frac{\mu(\Omega + S_x)}{\sqrt{(\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2}}, \quad (55)$$

$$\frac{\partial H_{11}}{\partial S_y} = \frac{\mu^2 S_y}{\sqrt{(\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2}}, \quad (56)$$

$$\begin{aligned} \frac{\partial H_{11}}{\partial S_z} &= S_z - c_2 b \\ &+ \frac{\mu(b + \mu S_z)}{\sqrt{(\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2}}. \end{aligned} \quad (57)$$

On the (1, 2) and (2, 1) surfaces one finds:

$$\frac{\partial H_{12}}{\partial S_x} = \frac{\partial H_{21}}{\partial S_x} = 0. \quad (58)$$

$$\frac{\partial H_{12}}{\partial S_y} = \frac{\partial H_{21}}{\partial S_y} = 0. \quad (59)$$

$$\frac{\partial H_{12}}{\partial S_z} = \frac{\partial H_{21}}{\partial S_z} = S_z - c_2 b, \quad (60)$$

while on the (2, 2) surface one finds:

$$\frac{\partial H_{22}}{\partial S_x} = -\frac{\mu(\Omega + S_x)}{\sqrt{(\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2}}, \quad (61)$$

$$\frac{\partial H_{22}}{\partial S_y} = -\frac{\mu^2 S_y}{\sqrt{(\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2}}, \quad (62)$$

$$\begin{aligned} \frac{\partial H_{22}}{\partial S_z} &= S_z - c_2 b \\ &- \frac{\mu(b + \mu S_z)}{\sqrt{(\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2}}. \end{aligned} \quad (63)$$

At this stage, in order to simplify the expression of the gradients of the adiabatic surface Hamiltonians, one can use the identity

$$\begin{aligned} (\Omega + \mu S_x)^2 + \mu^2 S_y^2 + (\mu S_z - c_1 b)^2 &= \Omega^2 + c_1^2 b^2 \\ &+ 2\mu(\Omega S_x - c_1 b S_z) + \mu^2 \mathbf{S}^2. \end{aligned} \quad (64)$$

As a matter of fact, the equations of motion (49-51) conserve the Casimir $\mathbf{S}^2 = S_M S_M$ for an arbitrary Hamiltonian $H_{\alpha\alpha'}$. To see this, one can rewrite the matrix \mathbf{B}^S in Eq. (12) as $\mathcal{B}_{IJ}^S = \epsilon_{IJK} S_K$ (where ϵ_{IJK} is the completely anti-symmetric tensor) and obtain

$$\begin{aligned} \frac{d}{dt} \mathbf{S}^2 &= \frac{\partial S_M S_M}{\partial S_I} \mathcal{B}_{IJ}^S \frac{\partial H_{\alpha\alpha'}}{\partial S_J} \\ &= -2\epsilon_{MIK} S_M S_K \frac{\partial H_{\alpha\alpha'}}{\partial S_J} = 0, \end{aligned} \quad (65)$$

where in the last step an odd permutations of the indices of ϵ_{KJM} has been performed. Since \mathbf{S}^2 is a constant of motion, one can define

$$C^2 = \Omega^2 + c_1^2 b^2 + \mu^2 \mathbf{S}^2, \quad (66)$$

so that

$$\tilde{\Omega}^2 + \gamma^2 + \eta^2 = C^2 + 2\mu(\Omega S_x - c_1 b S_z) . \quad (67)$$

Hence, the derivatives of the adiabatic surfaces can be rewritten as follows. On the (1, 1) surface one has:

$$\frac{\partial H_{11}}{\partial S_x} = \frac{\mu(\Omega + S_x)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} , \quad (68)$$

$$\frac{\partial H_{11}}{\partial S_y} = \frac{\mu^2 S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} , \quad (69)$$

$$\begin{aligned} \frac{\partial H_{11}}{\partial S_z} &= S_z - c_2 b \\ &+ \frac{\mu(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} . \end{aligned} \quad (70)$$

On the (1, 2) and (2, 1) surfaces one has:

$$\frac{\partial H_{12}}{\partial S_x} = \frac{\partial H_{21}}{\partial S_x} = 0 , \quad (71)$$

$$\frac{\partial H_{12}}{\partial S_y} = \frac{\partial H_{21}}{\partial S_y} = 0 , \quad (72)$$

$$\frac{\partial H_{12}}{\partial S_z} = \frac{\partial H_{21}}{\partial S_z} = S_z - c_2 b , \quad (73)$$

and on the (2, 2) surface one has:

$$\frac{\partial H_{22}}{\partial S_x} = -\frac{\mu(\Omega + S_x)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} , \quad (74)$$

$$\frac{\partial H_{22}}{\partial S_y} = -\frac{\mu^2 S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} , \quad (75)$$

$$\begin{aligned} \frac{\partial H_{22}}{\partial S_z} &= S_z - c_2 b \\ &- \frac{\mu(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} . \end{aligned} \quad (76)$$

V. TIME-REVERSIBLE INTEGRATORS

A different set of equations of motion corresponds to each adiabatic energy surface. Hence, one has to find different algorithms of integration on each surface. In the following, the Liouville propagator on each surface is factorized and the associated time-reversible algorithm for the spin dynamics is derived. It is worth noting that within a purely classical context other authors have considered alternative schemes of integration [56–58]. At the same time, while what follows is based on the basic symmetric Trotter factorization of the evolution operator, in order to integrate the spin dynamics, one could have used the elegant time-reversible measure-preserving algorithms invented by G. S. Ezra [47–49].

A. Reversible integrator on the (1, 1) adiabatic surface

The equations of motion on the (1, 1) surface can be written explicitly as

$$\begin{aligned} \dot{S}_x &= \frac{\mu^2 S_y S_z - \mu S_y (b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \\ &- S_y (S_z - c_2 b) , \end{aligned} \quad (77)$$

$$\begin{aligned}\dot{S}_y &= \frac{\mu S_x(b + \mu S_z) - \mu(\Omega + S_x)S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \\ &+ S_x(S_z - c_2 b) ,\end{aligned}\quad (78)$$

$$\dot{S}_z = \frac{\mu(\Omega + S_x)S_y - \mu^2 S_x S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} . \quad (79)$$

From Equations (77-79) one can easily find the corresponding Liouville operators

$$L_{1,(1,1)}^{S_x} = \frac{\mu^2 S_y S_z - \mu S_y(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \frac{\partial}{\partial S_x} , \quad (80)$$

$$L_{2,(1,1)}^{S_x} = -S_y(S_z - c_2 b) \frac{\partial}{\partial S_x} , \quad (81)$$

$$\begin{aligned}L_{(1,1)}^{S_y} &= \left[\frac{\mu S_x(b + \mu S_z) - \mu(\Omega + S_x)S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ &\quad \left. + S_x(S_z - c_2 b) \right] \frac{\partial}{\partial S_y} ,\end{aligned}\quad (82)$$

$$L_{(1,1)}^{S_z} = \frac{\mu(\Omega + S_x)S_y - \mu^2 S_x S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \frac{\partial}{\partial S_z} , \quad (83)$$

and the propagators

$$U_{1,(1,1)}^{S_x}(\tau) = \exp \left[\tau \frac{\mu^2 S_y S_z - \mu S_y(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \frac{\partial}{\partial S_x} \right] , \quad (84)$$

$$U_{2,(1,1)}^{S_x}(\tau) = \exp \left[-\tau S_y(S_z - c_2 b) \frac{\partial}{\partial S_x} \right] , \quad (85)$$

$$\begin{aligned}U_{(1,1)}^{S_y}(\tau) &= \exp \left\{ \tau \left[\frac{\mu S_x(b + \mu S_z) - \mu(\Omega + S_x)S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \right. \\ &\quad \left. \left. + S_x(S_z - c_2 b) \right] \frac{\partial}{\partial S_y} \right\} ,\end{aligned}\quad (86)$$

$$U_{(1,1)}^{S_z}(\tau) = \exp \left[\tau \frac{\mu(\Omega + S_x)S_y - \mu^2 S_x S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \frac{\partial}{\partial S_z} \right] . \quad (87)$$

The action of $U_{1,(1,1)}^{S_x}(\tau) = \exp[\tau L_{1,(1,1)}^{S_x}]$ on S_x can be found by means of the analytical integration of the equation of motion associated to the Liouville operator $L_{1,(1,1)}^{S_x}$ in Eq. (80). In pseudo-code form, one obtains

$$U_{1,(1,1)}^{S_x}(\tau) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \tau + [C_2 + C_1 S_x(0)]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ \quad - \frac{C_2}{C_1} , \end{cases} \quad (88)$$

where

$$C_1 = 2\mu\Omega , \quad (89)$$

$$C_2 = C^2 - 2\mu c_1 b S_z , \quad (90)$$

$$C_3 = \mu^2 S_y S_z - \mu S_y(b + \mu S_z) . \quad (91)$$

The actions of $U_{2,(1,1)}^{S_x}(\tau) = \exp[\tau L_{2,(1,1)}^{S_x}]$ and $U_{(1,1)}^{S_y}(\tau) = \exp[\tau L_{(1,1)}^{S_y}]$ on S_x and S_y , respectively, are simple variable shifts which can be written in pseudo-code form as

$$U_{2,(1,1)}^{S_x}(\tau) : \left\{ S_x \rightarrow S_x - \tau S_y(S_z - c_2 b) , \right. \quad (92)$$

$$U_{(1,1)}^{S_y}(\tau) : \begin{cases} S_y \rightarrow S_y + \tau \left[\frac{\mu S_x(b + \mu S_z) - \mu(\Omega + S_x)S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \quad \left. + S_x(S_z - c_2 b) \right]. \end{cases} \quad (93)$$

The action of $U_{(1,1)}^{S_z}(\tau) = \exp[\tau L_{(1,1)}^{S_z}]$ on S_z can also be determined by the analytical integration of the corresponding equation of motion

$$\dot{S}_z = \frac{\mu(\Omega + S_x)S_y - \mu^2 S_x S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} = \frac{B_3}{\sqrt{B_2 - B_1 S_z}}, \quad (94)$$

where one has defined

$$B_1 = 2\mu c_1 b, \quad (95)$$

$$B_2 = C^2 + 2\mu\Omega S_x, \quad (96)$$

$$B_3 = \mu(\Omega + S_x)S_y - \mu^2 S_x S_y. \quad (97)$$

One finds

$$U_{(1,1)}^{S_z}(\tau) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} \\ \quad - \frac{1}{B_1} \left\{ [B_2 - B_1 S_z]^{\frac{3}{2}} - \frac{3B_1 B_3 \tau}{2} \right\}^{\frac{2}{3}}. \end{cases} \quad (98)$$

Finally, one can consider three propagators on the (1, 1) surface:

$$\begin{aligned} U_{(1,1)}^1(\tau) &= U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) \\ &\times U_{(1,1)}^{S_y} \left(\frac{\tau}{2} \right) U_{(1,1)}^{S_z}(\tau) U_{(1,1)}^{S_y} \left(\frac{\tau}{2} \right) \\ &\times U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right), \end{aligned} \quad (99)$$

$$\begin{aligned} U_{(1,1)}^2(\tau) &= U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) \\ &\times U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) U_{(1,1)}^{S_y}(\tau) U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) \\ &\times U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right), \end{aligned} \quad (100)$$

$$\begin{aligned} U_{(1,1)}^3(\tau) &= U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) \\ &\times U_{1,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) U_{2,(1,1)}^{S_x}(\tau) U_{1,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) \\ &\times U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right), \end{aligned} \quad (101)$$

and write the corresponding integration algorithm. Each of the three propagators $U_{(1,1)}^k(\tau)$, $k = 1, \dots, 3$, can be used to obtain a different propagation algorithm. In order to obtain a more uniform sampling of phase space, one can also act with a different $U_{(1,1)}^k(\tau)$ at each successive time step τ .

B. Reversible integrator on the (2, 2) adiabatic surface

The equations of motion on the (2, 2) surface are

$$\dot{S}_x = \frac{\mu S_y(b + \mu S_z) - \mu^2 S_y S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}}$$

$$- S_y (S_z - c_2 b) , \quad (102)$$

$$\begin{aligned} \dot{S}_y &= \frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \\ &+ S_x (S_z - c_2 b) , \end{aligned} \quad (103)$$

$$\dot{S}_z = \frac{\mu^2 S_x S_y - \mu(\Omega + S_x)S_y}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} . \quad (104)$$

From Equations (102-104) one can easily write the corresponding Liouville operators

$$L_{1,(2,2)}^{S_x} = -\frac{C_3}{\sqrt{C_2 + C_1 S_x}} \frac{\partial}{\partial S_x} , \quad (105)$$

$$L_{2,(2,2)}^{S_x} = -S_y (S_z - c_2 b) \frac{\partial}{\partial S_x} , \quad (106)$$

$$\begin{aligned} L_{(2,2)}^{S_y} &= \left[\frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ &\quad \left. + S_x (S_z - c_2 b) \right] \frac{\partial}{\partial S_y} , \end{aligned} \quad (107)$$

$$L_{(2,2)}^{S_z} = -\frac{B_3}{\sqrt{B_2 - B_1 S_z}} \frac{\partial}{\partial S_z} , \quad (108)$$

where C_1, C_2, C_3 have been defined in Eqs. (89-91) and B_1, B_2, B_3 have been defined in Eqs. (95-97). The propagators for the (2,2) adiabatic surface can be written as

$$U_{1,(2,2)}^{S_x}(\tau) = \exp \left[-\tau \frac{C_3}{\sqrt{C_2 + C_1 S_x}} \frac{\partial}{\partial S_x} \right] , \quad (109)$$

$$U_{2,(2,2)}^{S_x}(\tau) = \exp \left[-\tau S_y (S_z - c_2 b) \frac{\partial}{\partial S_x} \right] , \quad (110)$$

$$\begin{aligned} U_{(2,2)}^{S_y}(\tau) &= \exp \left\{ \tau \left[\frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \right. \\ &\quad \left. \left. + S_x (S_z - c_2 b) \right] \frac{\partial}{\partial S_y} \right\} , \end{aligned} \quad (111)$$

$$U_{(2,2)}^{S_z}(\tau) = \exp \left[-\tau \frac{B_3}{\sqrt{B_2 - B_1 S_z}} \frac{\partial}{\partial S_z} \right] , \quad (112)$$

where C_1, C_2, C_3 have been defined in Eqs. (89-91) and B_1, B_2, B_3 have been defined in Eqs. (95-97).

The action of $U_{1,(2,2)}^{S_x}(\tau) = \exp[L_{1,(2,2)}^{S_x}]$ on S_x is determined by integrating analytically the equation of motion associated to the Liouville operator in (105). In pseudo-code form, such action can be written as

$$U_{1,(2,2)}^{S_x}(\tau) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \tau + (C_2 + C_1 S_x)^{3/2} \right]^{2/3} \\ - \frac{C_2}{C_1} . \end{cases} \quad (113)$$

Similarly, the action of $U_{(2,2)}^{S_z}(\tau) = \exp[L_{(2,2)}^{S_z}]$ on S_z is determined by integrating analytically the equation of motion associated to the Liouville operator in (108):

$$U_{(2,2)}^{S_z}(\tau) : \left\{ S_z \rightarrow \frac{B_2}{B_1} - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{3/2} + \frac{3}{2} B_1 B_3 \tau \right]^{2/3} . \right. \quad (114)$$

The propagators $U_{(2,2)}^{S_y}(\tau)$ and $U_{(2,2)}^{S_z}(\tau)$ generate simple time-shifts of the appropriate spin coordinates:

$$U_{2,(2,2)}^{S_x}(\tau) : \left\{ S_x \rightarrow S_x - \tau S_y (S_z - c_2 b) . \right. \quad (115)$$

$$U_{(2,2)}^{S_y}(\tau) : \begin{cases} S_y \rightarrow S_y + \tau \left[\frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x(S_z - c_2 b) \right]. \end{cases} \quad (116)$$

Finally, one can consider the following three propagators on the (2, 2) surface:

$$\begin{aligned} U_{(2,2)}^1(\tau) &= U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) U_{2,(2,2)}^{S_x}\left(\frac{\tau}{2}\right) U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) \\ &\times U_{(2,2)}^{S_y}\left(\frac{\tau}{2}\right) U_{(2,2)}^{S_z}(\tau) U_{(2,2)}^{S_y}\left(\frac{\tau}{2}\right) \\ &\times U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) U_{2,(2,2)}^{S_x}\left(\frac{\tau}{2}\right) U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right), \end{aligned} \quad (117)$$

$$\begin{aligned} U_{(2,2)}^2(\tau) &= U_{(2,2)}^{S_z}\left(\frac{\tau}{2}\right) U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) U_{2,(2,2)}^{S_x}\left(\frac{\tau}{2}\right) \\ &\times U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) U_{(2,2)}^{S_y}(\tau) U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) \\ &\times U_{2,(2,2)}^{S_x}\left(\frac{\tau}{2}\right) U_{1,(2,2)}^{S_x}\left(\frac{\tau}{4}\right) U_{(2,2)}^{S_z}\left(\frac{\tau}{2}\right), \end{aligned} \quad (118)$$

$$\begin{aligned} U_{(2,2)}^3(\tau) &= U_{(2,2)}^{S_y}\left(\frac{\tau}{4}\right) U_{(2,2)}^{S_z}\left(\frac{\tau}{2}\right) U_{(2,2)}^{S_y}\left(\frac{\tau}{4}\right) \\ &\times U_{1,(2,2)}^{S_x}\left(\frac{\tau}{2}\right) U_{2,(2,2)}^{S_x}(\tau) U_{1,(2,2)}^{S_x}\left(\frac{\tau}{2}\right) \\ &\times U_{(2,2)}^{S_y}\left(\frac{\tau}{4}\right) U_{(2,2)}^{S_z}\left(\frac{\tau}{2}\right) U_{(2,2)}^{S_y}\left(\frac{\tau}{4}\right), \end{aligned} \quad (119)$$

These allow one to find the algorithm of propagation on the (2, 2) surface. Each of the three propagators $U_{(2,2)}^k(\tau)$, $k = 1, \dots, 3$, can be used to obtain a different propagation algorithm. In order to obtain a more uniform sampling of phase space, one can also act with a different $U_{(2,2)}^k(\tau)$ at each successive time step τ .

C. Reversible integrators on the (1, 2) adiabatic surface

The equations of motion on the (1, 2) adiabatic energy surface are

$$\dot{S}_x = -S_y(S_z - c_2 b), \quad (120)$$

$$\dot{S}_y = S_x(S_z - c_2 b), \quad (121)$$

$$\dot{S}_z = 0. \quad (122)$$

They are identical to the equations of motion on the (2, 1) energy surface. The Liouville operators associated to the Eqs. (120) and (121) are:

$$L_{(1,2)}^{S_x} = -S_y(S_z - c_2 b) \frac{\partial}{\partial S_x}, \quad (123)$$

$$L_{(1,2)}^{S_y} = S_x(S_z - c_2 b) \frac{\partial}{\partial S_y}. \quad (124)$$

The associated propagators are:

$$U_{(1,2)}^{S_x}(\tau) = \exp \left[-\tau S_y(S_z - c_2 b) \frac{\partial}{\partial S_x} \right], \quad (125)$$

$$U_{(1,2)}^{S_y}(\tau) = \exp \left[\tau S_x(S_z - c_2 b) \frac{\partial}{\partial S_y} \right]. \quad (126)$$

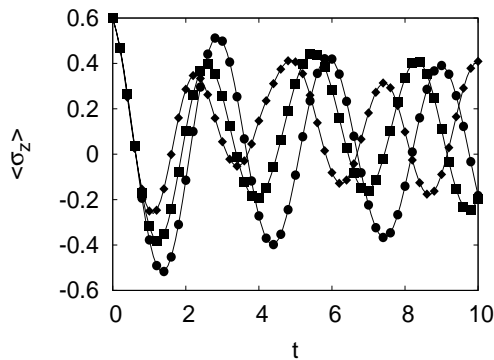


FIG. 1: Time evolution of the population difference $\langle \sigma_z(t) \rangle$ for $\beta = 0.3$, $\Omega = 1$, $b = 1$, $c_1 = 0.01$, $c_2 = 0.1$. The coefficient μ takes the values 0.25, 0.5 and 0.74 for black circles, squares and diamonds, respectively. The lines are drawn to help the eye.

Finally, one can consider the following total propagators on the $(1, 2)$ surface:

$$U_{(1,2)}^1(\tau) = U_{(1,2)}^{S_x}\left(\frac{\tau}{2}\right) U_{(1,2)}^{S_y}(\tau) U_{(1,2)}^{S_x}\left(\frac{\tau}{2}\right), \quad (127)$$

$$U_{(1,2)}^2(\tau) = U_{(1,2)}^{S_y}\left(\frac{\tau}{2}\right) U_{(1,2)}^{S_x}(\tau) U_{(1,2)}^{S_y}\left(\frac{\tau}{2}\right), \quad (128)$$

and easily write the algorithm of integration. Each of the two propagators $U_{(1,2)}^k(\tau)$, $k = 1, 2$, can be used to obtain a different propagation algorithm. In order to obtain a more uniform sampling of phase space, one can also act with a different $U_{(1,2)}^k(\tau)$ at each successive time step τ .

VI. NUMERICAL RESULTS

In order to analyze the quantum dynamics of the model, one can calculate averages in the Heisenberg-like picture:

$$\langle \hat{\chi} \rangle_t = \sum_{\alpha\alpha'} \int d^3\mathbf{S} \rho_{\alpha\alpha'}(\mathbf{S}) \chi_{\alpha'\alpha}(\mathbf{S}, t) \quad (129)$$

where $\hat{\chi}(\mathbf{S}, t)$ is the chosen observable (which is evolved in time), also depending on the classical spin coordinates $\mathbf{S} = (S_x, S_y, S_z)$, and $d^3\mathbf{S} = dS_x dS_y dS_z$. For the sake of illustrating the integration algorithms derived in Sec. V, it is assumed that at time $t = 0$ the spin and the quantum systems are decoupled so that the initial density matrix is

$$\hat{\rho}(\mathbf{S}) = \hat{\rho}_s \otimes \sqrt{\frac{\beta}{2\pi}} \exp[-\beta S_z^2], \quad (130)$$

where $\hat{\rho}_s$ is the density matrix of the isolated quantum subsystem. In order to study the evolution of both the population difference between the excited and ground state of the model and the coherence of the initial superposition between such states, it is assumed that the quantum subsystem is in a superposition of states at $t = 0$ that is represented in the basis of σ_z by the state vector

$$|\Psi\rangle = \frac{\sqrt{5}}{5} [2|1\rangle - |2\rangle]. \quad (131)$$

The associated density matrix has components

$$\rho_s = \begin{bmatrix} 4/5 & -2/5 \\ -2/5 & 1/5 \end{bmatrix}. \quad (132)$$

According to such choices, the dynamics will display both population and coherence oscillations. The density matrix in the adiabatic basis takes the form

$$\rho_s^{\text{ad}} = \frac{1}{\mathcal{N}} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & \rho_{22} \end{bmatrix}, \quad (133)$$

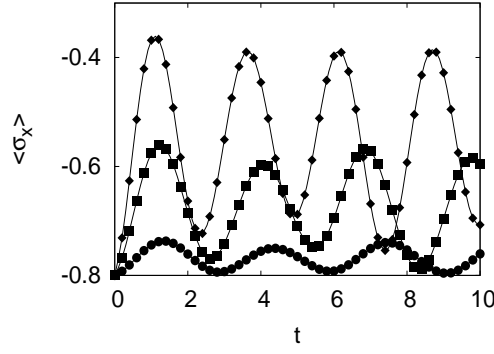


FIG. 2: Time evolution of the coherence $\langle \sigma_x(t) \rangle$ for $\beta = 0.3, \Omega = 1, b = 1, c_1 = 0.01, c_2 = 0.1$. The coefficient μ takes the values 0.25, 0.5 and 0.74 for black circles, squares and diamonds, respectively. The lines are drawn to help the eye.

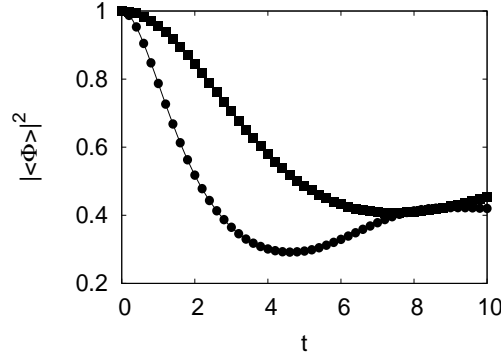


FIG. 3: Time evolution of the modulus square of the average phase for $\beta = 0.3, \Omega = 1, b = 1, c_1 = 0.01, c_2 = 0.1, \mu = 0.25$; the black circles denote the results for the geometric phase while the black squares denote the results for the Bohr phase.

where, using the definition of G given in Eq. (47),

$$\rho_{11} = \frac{1}{5} \left[\frac{9\eta^2}{\gamma^2} + (3 + G)^2 \right], \quad (134)$$

$$\rho_{22} = \frac{1}{5} \left[\frac{\eta^2}{\gamma^2} + (1 - G)^2 \right], \quad (135)$$

$$\rho_{12} = -\frac{[3i\eta + \gamma(3 + G)][-i\eta + \gamma(-1 + 3G)]}{5\gamma^2}, \quad (136)$$

$$\mathcal{N} = 2(1 + G^2 + \eta^2/\gamma^2). \quad (137)$$

One can use spherical coordinates

$$S_x = S \sin(\theta) \cos(\phi) \quad (138)$$

$$S_y = S \sin(\phi) \sin(\theta) \quad (139)$$

$$S_z = S \cos(\theta) \quad (140)$$

in order to sample the Boltzmann weight on S_z as

$$\exp \left[-\beta \frac{S_z^2}{2} \right] = \exp \left[-\beta \frac{\cos^2 \theta}{2} \right] \quad (141)$$

by sampling $\cos(\theta)$ uniformly between $(-1, 1)$ and to sample the angle ϕ uniformly between $(0, 2\pi)$. The observables $\sigma_z(\mathbf{S}, t)$ and $\sigma_x(\mathbf{S}, t)$ are evolved in the adiabatic basis and the calculation of their trace, according to Eq. (129), provides the population and the coherence evolution, respectively.

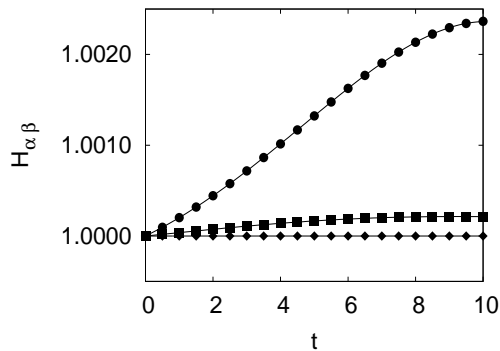


FIG. 4: Adiabatic surface Hamiltonians vs time. The black circles denote the curve for $\alpha = 1$ and $\beta = 1$ (excited state dynamics); the square denote the curve for $\alpha = 2$ and $\beta = 2$ (ground state dynamics) while the black diamonds denote the curve $\alpha = 1$ and $\beta = 2$ (mean surface dynamics). The continuous line are for helping the eye. The parameters specifying the calculations are $\beta = 0.3$, $\Omega = 1$, $b = 1$, $c_1 = 0.01$, $c_2 = 0.1$, $\mu = 0.75$. the black circles denote the results for the geometric phase while the black

Calculations were performed for $\beta = 0.3$, $\Omega = 1$, $b = 1$, $c_1 = 0.01$, $c_2 = 0.1$. The coefficient μ was varied and took the values 0.25, 0.5 and 0.74. The values of the parameters are given in dimensionless units. Figure 1 shows the behavior of the population as a function of time when the coupling μ is varied. The damping increases as the coupling increases. Figure 2 displays the time evolution of the coherence when the coupling is varied. The coherence oscillations are greater for greater coupling. Since the two-level system is coupled to a single rotating classical spin, no real dissipation is expected when monitoring the dynamics of the two-level system only. In Figure 3 the time evolution of the moduli square of the average of the Bohr and geometric phases are shown. No major geometric effect was expected for the model studied. Finally, the stability of the integration algorithm introduced in Sec. (V) is illustrated in Fig. (4). A numerical integration time step $\tau = 0.001$ (in dimensionless units) was used in all the calculation performed. The Trotter symmetric factorization discussed in Sec. (V) was combined with a fifth order Yoshida scheme [59]. As expected, the more stable numerical integration is achieved on the (1, 2) mean energy surface. This arises from the absence of quantum effects on the mean surface of the model in Eq. (39). As quantum effects increase, going from the ground state (2, 2) to the excited state (1, 1), the stability of the numerical integration somewhat diminishes but remains satisfactory over the whole time interval explored. The numerical conservation of the spin modulus is almost perfect on all the three adiabatic energy surfaces.

VII. CONCLUSIONS AND PERSPECTIVES

In this paper a formalism for studying the dynamics of quantum systems coupled to classical spin environments has been reviewed. The theory is based on generalized antisymmetric brackets and naturally predicts the existence of open-path off-diagonal geometric phases in the dynamics of the density matrix. It has also been shown that such geometric phases must be considered in the quantum-classical Liouville equation, expressed by means of canonical phase space coordinates, whenever the adiabatics basis is complex (as in the case of a magnetic field coupled to the quantum subsystem).

When the quantum subsystem is weakly coupled to the spin environment, non-adiabatic transitions can be neglected. In such a case, one can construct an effective non-Markovian computer simulation scheme for open quantum system dynamics in a classical spin environment. In this paper a detailed derivation of integration algorithms based on the symmetric Trotter factorization of the classical-like spin propagator has been given. Such algorithms have been applied to a model system comprising a quantum two-level system coupled to a single classical spin in an external magnetic field. The numerical integration conserves the spin modulus perfectly and the spin energy satisfactorily during the entire time interval explored. Starting from an excited state, the population difference and the coherences of the two-state model have been simulated and studied in function of the strength of the coupling parameter between the spin and the two-level system.

One could look at the numerical evidence provided in this paper as a first step toward developing the simulation schemes for quantum dynamics in classical spin environments into an effective tool for studying systems of interest in nano-science.

Appendix A: Integration algorithm on the (1, 1) surface

In pseudo-code form, the algorithm provided by $U_{(1,1)}^1(\tau)$ is:

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A1})$$

$$U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right\}, \quad (\text{A2})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A3})$$

$$U_{(1,1)}^{S_y} \left(\frac{\tau}{2} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{2} \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{A4})$$

$$U_{(1,1)}^{S_z}(\tau) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} \right. \\ \left. - \frac{3B_1 B_3 \tau}{2} \right]^{\frac{2}{3}}, \end{cases} \quad (\text{A5})$$

$$U_{(1,1)}^{S_y} \left(\frac{\tau}{2} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{2} \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{A6})$$

$$U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right\}, \quad (\text{A7})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A8})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}. \end{cases} \quad (\text{A9})$$

The algorithm provided by $U_{(1,1)}^2(\tau)$ is:

$$U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left\{ [B_2 - B_1 S_z]^{\frac{3}{2}} - \frac{3B_1 B_3 \tau}{4} \right\}^{\frac{2}{3}}, \end{cases} \quad (\text{A10})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A11})$$

$$U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right\}, \quad (\text{A12})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A13})$$

$$U_{(1,1)}^{S_y}(\tau) : \begin{cases} S_y \rightarrow S_y + \tau \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{A14})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A15})$$

$$U_{2,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right\}, \quad (\text{A16})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{4} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{4} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A17})$$

$$U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left\{ [B_2 - B_1 S_z]^{\frac{3}{2}} - \frac{3B_1 B_3 \tau}{4} \right\}^{\frac{2}{3}}. \end{cases} \quad (\text{A18})$$

The algorithm provided by $U_{(1,1)}^3(\tau)$ is:

$$U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{A19})$$

$$U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} - \frac{3B_1 B_3 \tau}{4} \right]^{\frac{2}{3}}, \end{cases} \quad (\text{A20})$$

$$U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{A21})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{2} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A22})$$

$$U_{2,(1,1)}^{S_x}(\tau) : \{ S_x \rightarrow S_x - \tau S_y (S_z - c_2 b) \}, \quad (\text{A23})$$

$$U_{1,(1,1)}^{S_x} \left(\frac{\tau}{2} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left\{ \frac{3}{2} C_1 C_3 \frac{\tau}{2} + [C_2 + C_1 S_x]^{\frac{3}{2}} \right\}^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{A24})$$

$$U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right] , \end{array} \right. \quad (\text{A25})$$

$$U_{(1,1)}^{S_z} \left(\frac{\tau}{2} \right) : \left\{ \begin{array}{l} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} - \frac{3B_1 B_3 \tau}{4} \right]^{\frac{2}{3}} , \end{array} \right. \quad (\text{A26})$$

$$U_{(1,1)}^{S_y} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu S_x (b + \mu S_z) - \mu (\Omega + S_x) S_z}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right] . \end{array} \right. \quad (\text{A27})$$

Appendix B: Integration algorithm on the (2, 2) surface

The algorithm provided by $U_{(2,2)}^1(\tau)$ is

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} , \end{array} \right. \quad (\text{B1})$$

$$U_{2,(2,2)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) , \right. \quad (\text{B2})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} , \end{array} \right. \quad (\text{B3})$$

$$U_{(2,2)}^{S_y} \left(\frac{\tau}{2} \right) : \left\{ \begin{array}{l} S_y \rightarrow S_y + \frac{\tau}{2} \left[\frac{\mu (\Omega + S_x) S_z - \mu S_x (b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right] , \end{array} \right. \quad (\text{B4})$$

$$U_{(2,2)}^{S_z}(\tau) : \left\{ \begin{array}{l} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} + \frac{3}{2} B_1 B_3 \tau \right]^{\frac{2}{3}} , \end{array} \right. \quad (\text{B5})$$

$$U_{(2,2)}^{S_y} \left(\frac{\tau}{2} \right) : \left\{ \begin{array}{l} S_y \rightarrow S_y + \frac{\tau}{2} \left[\frac{\mu (\Omega + S_x) S_z - \mu S_x (b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right] , \end{array} \right. \quad (\text{B6})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} , \end{array} \right. \quad (\text{B7})$$

$$U_{2,(2,2)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right. , \quad (\text{B8})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} \end{array} \right. . \quad (\text{B9})$$

The algorithm provided by $U_{(2,2)}^2(\tau)$ is

$$U_{(2,2)}^{S_z} \left(\frac{\tau}{2} \right) : \left\{ \begin{array}{l} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} + \frac{3}{2} B_1 B_3 \frac{\tau}{2} \right]^{\frac{2}{3}} \end{array} \right. , \quad (\text{B10})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} \end{array} \right. , \quad (\text{B11})$$

$$U_{2,(2,2)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right. , \quad (\text{B12})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} \end{array} \right. , \quad (\text{B13})$$

$$U_{(2,2)}^{S_y}(\tau) : \left\{ \begin{array}{l} S_y \rightarrow S_y + \tau \left[\frac{\mu(\Omega + S_x) S_z - \mu S_x (b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right] \end{array} \right. , \quad (\text{B14})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} \end{array} \right. , \quad (\text{B15})$$

$$U_{2,(2,2)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right. , \quad (\text{B16})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{4} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1} \end{array} \right. , \quad (\text{B17})$$

$$U_{(2,2)}^{S_z} \left(\frac{\tau}{2} \right) : \left\{ \begin{array}{l} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{3/2} + \frac{3}{2} B_1 B_3 \frac{\tau}{2} \right]^{2/3} \end{array} \right. . \quad (\text{B18})$$

The algorithm provided by $U_{(2,2)}^3(\tau)$ is

$$U_{(2,2)}^{S_y} \left(\frac{\tau}{4} \right) : \left\{ \begin{array}{l} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu(\Omega + S_x) S_z - \mu S_x (b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right] \end{array} \right. , \quad (\text{B19})$$

$$U_{(2,2)}^{S_z} \left(\frac{\tau}{2} \right) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} + \frac{3}{2} B_1 B_3 \frac{\tau}{2} \right]^{\frac{2}{3}} \end{cases}, \quad (\text{B20})$$

$$U_{(2,2)}^{S_y} \left(\frac{\tau}{4} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{B21})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{2} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{2} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{B22})$$

$$U_{2,(2,2)}^{S_x}(\tau) : \{S_x \rightarrow S_x - \tau S_y (S_z - c_2 b) \}, \quad (\text{B23})$$

$$U_{1,(2,2)}^{S_x} \left(\frac{\tau}{2} \right) : \begin{cases} S_x \rightarrow \frac{1}{C_1} \left[-\frac{3}{2} C_1 C_3 \frac{\tau}{2} + (C_2 + C_1 S_x)^{\frac{3}{2}} \right]^{\frac{2}{3}} \\ - \frac{C_2}{C_1}, \end{cases} \quad (\text{B24})$$

$$U_{(2,2)}^{S_y} \left(\frac{\tau}{4} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right], \end{cases} \quad (\text{B25})$$

$$U_{(2,2)}^{S_z} \left(\frac{\tau}{2} \right) : \begin{cases} S_z \rightarrow \frac{B_2}{B_1} \\ - \frac{1}{B_1} \left[(B_2 - B_1 S_z)^{\frac{3}{2}} + \frac{3}{2} B_1 B_3 \frac{\tau}{2} \right]^{\frac{2}{3}} \end{cases}, \quad (\text{B26})$$

$$U_{(2,2)}^{S_y} \left(\frac{\tau}{4} \right) : \begin{cases} S_y \rightarrow S_y + \frac{\tau}{4} \left[\frac{\mu(\Omega + S_x)S_z - \mu S_x(b + \mu S_z)}{\sqrt{C^2 + 2\mu(\Omega S_x - c_1 b S_z)}} \right. \\ \left. + S_x (S_z - c_2 b) \right]. \end{cases} \quad (\text{B27})$$

Appendix C: Integration algorithm on the (1, 2) surface

The algorithm provided by $U_{(1,2)}^1(\tau)$ is

$$U_{(1,2)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right\}, \quad (\text{C1})$$

$$U_{(1,2)}^{S_y}(\tau) : \{S_y \rightarrow S_y + \tau S_x (S_z - c_2 b) \}, \quad (\text{C2})$$

$$U_{(1,2)}^{S_x} \left(\frac{\tau}{2} \right) : \left\{ S_x \rightarrow S_x - \frac{\tau}{2} S_y (S_z - c_2 b) \right\}. \quad (\text{C3})$$

The algorithm provided by $U_{(1,2)}^2(\tau)$ is

$$U_{(1,2)}^{S_y} \left(\frac{\tau}{2} \right) : \left\{ S_y \rightarrow S_y + \frac{\tau}{2} S_x (S_z - c_2 b) \right\}, \quad (\text{C4})$$

$$U_{(1,2)}^{S_x}(\tau) : \{S_x \rightarrow S_x - \tau S_y (S_z - c_2 b) \}, \quad (\text{C5})$$

$$U_{(1,2)}^{S_y} \left(\frac{\tau}{2} \right) : \left\{ S_y \rightarrow S_y + \frac{\tau}{2} S_x (S_z - c_2 b) \right\}. \quad (\text{C6})$$

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